

Relative importance of model and parameter uncertainty in models used for prediction of persistence and long-range transport potential of chemical pollutants

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Abstract: Overall persistence (P_{OV}) and long-range transport potential (LRTP) of chemicals are two indicators used in the context of precautionary chemical assessment. Multimedia fate models are used in research and regulatory contexts to calculate numerical indicators of P_{OV} and LRTP. The resulting indicator values exhibit uncertainty due to model uncertainty concerning model design and due to type A and B parameter uncertainty in the substance parameters. In this study, we compare the relative magnitude of parameter and model uncertainty for a large set of 3175 hypothetical chemicals that evenly cover the chemical parameter space and for eight different multimedia models available for the calculation of P_{OV} and LRTP. The assessment of the relative magnitude of the two types of uncertainty is important to direct further research and to inform the user on the level of confidence he can have in the model results. It is shown that, for P_{OV} , parameter uncertainty is larger than model uncertainty in most cases (78%), and that model uncertainty becomes more important for those chemicals which partition in considerable amounts into more than one environmental compartment. For LRTP, on the other hand, model uncertainty is higher than parameter uncertainty in most cases (75%). This dominance of model uncertainty can be explained with known differences in the model features. Uncertainty of P_{OV} can thus be reduced most effectively by improving data on degradation rate constants. For LRTP, the choice of the model that is best suited for the assessment purpose in question is most essential to reduce uncertainty.

Keywords: Uncertainty analysis; Multimedia model; Exposure analysis

1. INTRODUCTION

High overall persistence (P_{OV}) and long-range transport potential (LRTP) have been recognized as hazardous characteristics for chemicals that might be released to the environment (e.g., Scheringer, 1996). Numerical indicators of P_{OV} and LRTP are therefore used in various contexts for the assessment of the hazard posed to the environment by chemicals, e.g. for identifying candidate persistent organic pollutants (POPs) within the Stockholm Convention (UNEP, 2000). However, it is difficult to directly measure these

two descriptors of chemical fate in the environment.

Multimedia models have been found to be appropriate tools for calculating numerical values for P_{OV} and LRTP. The results of these calculations are subject to two main types of uncertainties. First, they are influenced by parameter uncertainty due to uncertainty in the measurement methods for chemical substance properties as well as natural variability of the environmental parameters within the large areas covered by the multimedia models. The second major uncertainty is due to differences between the various multimedia models available for the

calculation of P_{OV} and LRTP. Because the original goals and motivations for developing these models were different, they exhibit differences in the model geometry, parameterization of the environment and also use different definitions of the endpoints P_{OV} and LRTP. Differences in P_{OV} and LRTP due to model design are here referred to as model uncertainty.

Because of the potential application of these models in regulatory decisions, assessing the magnitude and relative importance of the two types of uncertainty needs to be an area of active research. Work on quantifying the influence of parameter uncertainty on P_{OV} and LRTP has been conducted by Bennett et al. (2001), Beyer and Matthies (2002) and Fenner et al. (2004). In these studies, 30 to 70 compounds with diverse partitioning behavior have been investigated. All three studies used Monte Carlo simulations to determine 80 to 90% confidence intervals of the results. These confidence intervals were found to typically span factors between 5-30 for P_{OV} and between 2-50 for LRTP.

Model comparison studies, on the other hand, have been conducted by Wania and co-workers (WECC, 2000; Wania and Dugani, 2003), and Bennett et al. (2001), and are currently being conducted by an OECD expert group (OECD, 2004). Their findings indicate that rankings in terms of P_{OV} and LRTP of broad sets of different chemicals are broadly similar across different models (i.e., rank correlation coefficients are regularly > 0.9 among models). For P_{OV} , good correlations even for the absolute results have been found among different models. The model comparisons have also shown that significant discrepancies between the models occur only for identifiable combinations of partitioning characteristics and degradation rate constants. These discrepancies are directly attributable to basic differences in the models, for example, consideration of transport in air only versus coupled transport in air and water.

In none of these studies, however, have the relative magnitudes of model and parameter uncertainty been compared. Such a comparison is required to direct further research and to supply the model users with information on the degree of confidence they can have in the model results and on how to use the results in the assessment of substances. The model comparison study of the OECD expert group, in which P_{OV} and LRTP of 3175 hypothetical chemicals that span a large range of chemical properties were compared for nine different models, provides a unique opportunity to conduct such a comparison of model and parameter uncertainty. Here, we present an assessment of parameter uncertainty in

P_{OV} and LRTP for these same 3175 chemicals for two distinctly different models, ChemRange and ELPOS. We then compare the uncertainty ranges spanned by eight of the models with the uncertainty ranges due to parameter uncertainty in the two models for each of the 3175 chemicals.

Our objective is to assess the relative magnitude of parameter versus model uncertainty for different chemical property combinations and for the two indicators P_{OV} and LRTP. In this way, we learn when further research should focus on the reduction of parameter uncertainty and variability and when it should rather focus on model optimization.

2 METHODS

2.1 Models and definitions of P_{OV} and LRTP

To assess model uncertainty, results from 8 out of the 9 models in the OECD study (OECD, 2004) were compared (see Figure 1). GloboPOP is not included here because it is not applicable to the full range of chemical property combinations investigated with the other models. The eight models share a set of common characteristics: All are based on a mass balance approach, have a compartmental design and rely on empirical sub-models to describe partitioning between various environmental compartments and sub-compartments. However, the models also differ considerably in several respects. These include different compartment geometries, different numbers and types of compartments included, processes that are only present in a subset of models and the degree of spatial resolution of the models. The differences between the models are described in more detail in OECD (2004).

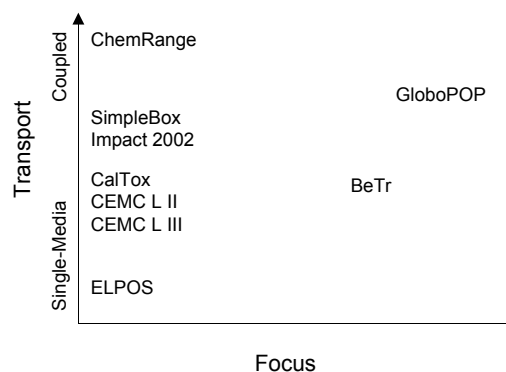


Figure 1. Comparison of multimedia models with respect to mode of transport (single-medium vs. coupled, vertical axis) and LRTP metric (transport- or target-region oriented, horizontal axis).

Two main distinctions are particularly influential in the hazard indicators calculated by the models. First, the models differ with respect to whether they allow for long-range transport in both air and water and to what extent these two transport mechanisms are coupled. In the extreme, ChemRange calculates fully coupled air-water transport, while ELPOS calculates separate air and water transport potentials. Second, while the models agree in their definition of P_{OV} (i.e., the chemical's reactive residence time in the system), they may differ with respect to the way in which LRTP is calculated. A main distinction is between BETR-GLTE, on the one hand, and all other models, on the other hand. The LRTP metric of BETR-GLTE describes the degree of deposition to the surface media in target regions after transport in air ("target-region focused"). The LRTP metrics of the other models describe the potential for transport in the mobile media air and/or water without deposition to the surface media ("transport-focused"). These different transport metrics can cause major differences between model results for LRTP.

2.2 Hypothetical chemicals and parameter uncertainty

Since the relative magnitude of parameter and model uncertainty might vary with the partitioning and degradation properties of a chemical, the comparison was conducted for a set of hypothetical chemicals ($n = 3175$) covering a broad part of the "chemical space". The "chemical space" represents the entire range of plausible combinations of relative solubilities between air, water and octanol, with octanol chosen as a surrogate for sorptive phases such as soils, sediments and aerosols. By choosing hypothetical instead of real chemicals, we circumvent the issue of data reliability and at the same time achieve and even coverage of the possible range of applicability of the models.

The hypothetical chemicals are the same as used in OECD (2004) and were constructed as follows: $\log K_{aw}$ values were varied from -11 to 2 and $\log K_{oa}$ values from -1 to 15 in steps of one logarithmic unit. All possible combinations were formed with the restriction of $8 \geq \log K_{oa} + \log K_{aw} = \log K_{ow} \geq -1$ (K_{aw} : air-water partition coefficient, K_{oa} : octanol-air partition coefficient, K_{ow} : octanol-water partition coefficient). An additional dimension of chemical properties was added by defining five half-life categories ranging from 24 hours to 87,600 hours (10 years) for soil, water and sediment and five categories for half-lives in air ranging from 4 hours to 8760 hours (1 year).

To limit the number of possible combinations to an acceptable level, half-lives in soil were set to twice the half-lives in water, and half-lives in sediment were set to ten times those in water. These 25 half-life combinations were then combined with all of the 127 possible combinations of partition coefficients to yield 3175 hypothetical chemicals.

To assess the degree of parameter uncertainty in the resulting P_{OV} and LRTP values of each chemical, substance-specific input parameters (partition coefficients and degradation rate constants) were varied for each hypothetical chemical. Identical uncertainty factors were assumed for all chemicals. They were chosen to be a factor of 10 for degradation rate constants and a factor of 3 for partition coefficients. Factors of similar magnitude have been found for data for real chemicals (e.g., Fenner, 2001; Webster et al., 1998; McKone, 1993). Each hypothetical chemical was then represented as 32 realizations by individually multiplying or dividing each substance-specific input parameter by the square root of the uncertainty factor. This leads to 2 values for each of the two partition coefficients and three degradation rate constants, yielding $2^5=32$ combinations for each chemical.

2.3 Comparing parameter and model uncertainty

To assess parameter uncertainty in P_{OV} and LRTP, the 32 realizations of each of the 3175 hypothetical chemicals were run through ChemRange and ELPOS. These two models were selected for assessment of parameter uncertainty as examples of two distinctly different models. Parameter uncertainties determined for these two models are expected to be representative of all 8 models in the exercise. For calculation of the model uncertainty, the eight models were run for all 3175 hypothetical chemicals and P_{OV} and LRTP for each chemical from each model was determined. In all calculations, emission to air was assumed.

The comparison of parameter to model uncertainty has to be conducted differently for P_{OV} and LRTP. Since all models use the same definition of P_{OV} , uncertainty in P_{OV} among models can be assessed directly for the absolute results of P_{OV} (given in days). The extent of uncertainty among the eight models and over the 32 chemical realizations is determined by calculating coefficients of variation ($CV = \text{standard deviation/mean}$) for each hypothetical chemical. The relative magnitude of parameter versus model uncertainty for each chemical x

(uncertainty ratio, UR_{Pov}^x) was then determined as the ratio of the CV due to parameter uncertainty ($CV_{Pov,para}^x$) and the CV due to model uncertainty ($CV_{Pov,model}^x$).

$$UR_{Pov}^x = CV_{Pov,para}^x / CV_{Pov,model}^x \quad (1)$$

In this way, 3175 UR_{Pov}^x values, covering the entire chemical space, were calculated.

For LRTP, model results cannot be compared in terms of absolute LRTP values, due to different definitions and therefore also different LRTP metrics. In order to compare the LRTP model results, we determine the rank of a chemical's LRTP value within the list of 3175 chemicals. In this way it is possible to compare the LRTP results among different models. The standard deviation (STD) of ranks is already a normalized measure. Therefore, model uncertainty can be quantified by calculating the STD of the LRTP rank of each hypothetical chemical over the different models (without dividing the STD by the mean of the ranks). To assess parameter uncertainty, the same measure was calculated, i.e. the STD of the rankings of each chemical when its substance-properties are varied according to the 32 realizations while the properties of all other 3174 chemicals are kept at their base case values. Accordingly, the relative magnitude of parameter versus model uncertainty (UR_{LRTP}^x) is determined as the ratio of the STD due to parameter uncertainty ($STD_{LRTP,para}^x$) and the STD due to model uncertainty ($STD_{LRTP,model}^x$).

$$UR_{LRTP}^x = STD_{LRTP,para}^x / STD_{LRTP,model}^x \quad (2)$$

In this way, 3175 UR_{LRTP}^x values, covering the entire chemical space, were calculated.

3 RESULTS AND DISCUSSION

In Table 1, the percentage of the 3175 hypothetical chemicals for which the parameter uncertainty is smaller than the model uncertainty is given. In the case of P_{OV} the parameter uncertainty seems to dominate in most cases, i.e., in only 22% of the cases in ChemRange and in only 17% of the cases in ELPOS is parameter uncertainty smaller than model uncertainty. For LRTP, in contrast, the model uncertainty seems to dominate in most cases, i.e. in 75% of the cases in ChemRange and in 81% of the cases in ELPOS. Although the percentages for the two models are not identical in Table 1, they indicate the same trend.

Table 1. Percentage of uncertainty ratios smaller than 1, i.e. percentage of chemicals for which model uncertainty is larger than parameter uncertainty for the two models ChemRange and ELPOS and for the indicators P_{OV} and LRTP.

	ChemRange	ELPOS
$UR_{Pov}^x < 1$	21.7	16.9
$UR_{LRTP}^x < 1$	75.2	81.0

In addition to the information in Table 1, Figures 2 and 3 give the frequency distributions of the uncertainty ratios UR_{Pov}^x and UR_{LRTP}^x in the models ChemRange and ELPOS. For P_{OV} the frequency distributions of the two models are very similar. The P_{OV} uncertainty ratios reach values up to 30, indicating parameter uncertainty far dominates model uncertainty for some chemical property combinations. For LRTP, the two frequency distributions are also similar in shape and give the same general picture, i.e. high frequencies below 1 and frequencies close to 0 above 2. Model uncertainty therefore clearly dominates.

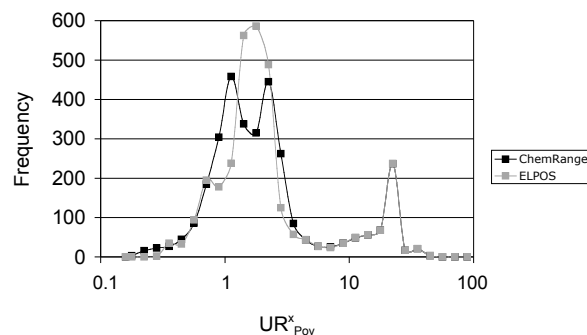


Figure 2. Frequency distributions of UR_{Pov}^x in ChemRange and ELPOS.

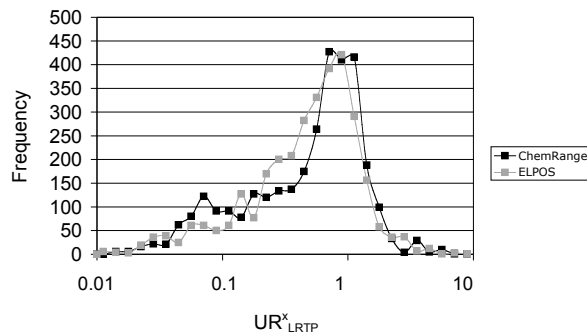


Figure 3. Frequency distributions of UR_{LRTP}^x in ChemRange and ELPOS.

To better understand how the frequencies of higher model than parameter uncertainty relate to chemical properties and to learn why model

uncertainty dominates for LRTP for the majority of chemical property combinations while for P_{OV} the opposite is the case, we have further analyzed how those incidences of $UR_{POV}^x < 1$ and $UR_{LRTP}^x < 1$ are distributed in the chemical space. Figure 4 shows a contour plot which gives the number of incidences with $UR_{POV}^x < 1$ in the K_{oa} - K_{aw} -space for ChemRange. Figure 5 depicts the same contour plot for LRTP, i.e. it shows the number of incidences for which $UR_{LRTP}^x < 1$ in the K_{oa} - K_{aw} -space for ChemRange. Low numerical values in these plots indicate areas of the chemical space where parameter uncertainty dominates model uncertainty.

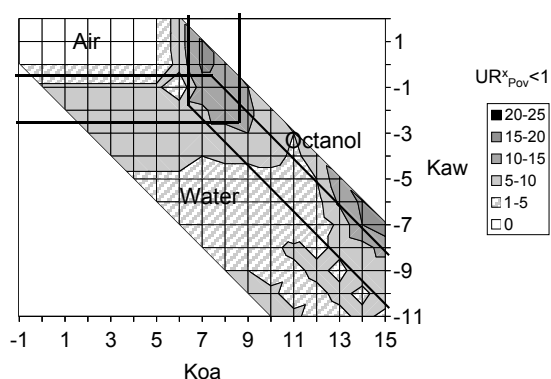


Figure 4. Distribution of number of incidences with $UR_{POV}^x < 1$ in the chemical space spanned by K_{oa} and K_{aw} (results for ChemRange). Lines are drawn to delimit property combinations for which $>90\%$ of the chemical will be present in one compartment only.

For P_{OV} , regions with the smallest numbers of $UR_{POV}^x < 1$, i.e. with a large number of cases for which parameter uncertainty dominates over model uncertainty, are those regions where the chemicals partition mainly into one compartment (see Figure 4). It can further be found that while the parameter uncertainty stays relatively constant at a high level ($CV=0.7-0.85$) in most regions, the model uncertainty varies to larger extents ($CV=0.03-2$). Whether parameter or model uncertainty dominates for a certain chemicals is therefore mainly determined by the extent of model uncertainty. In areas where the chemical partitions in considerable amounts between two or three media, model uncertainty becomes larger and might exceed parameter uncertainty more frequently. There is one region at low K_{aw} values and high K_{oa} values that deviates from this rule and that can be shown to have very low parameter uncertainties for certain chemical property combinations ($CV=0.2-0.6$). This is a region in chemical space where chemicals in air are present

almost exclusively bound to particles. It is then the dynamics of particle deposition processes that determine P_{OV} rather than the half-lives in the main compartments. Since no uncertainty has been assumed for the processes responsible for particle dynamics, parameter uncertainty is very low for particle-bound chemicals.

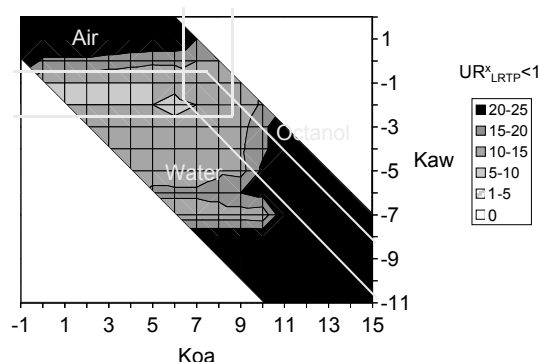


Figure 5. Distribution of number of incidences with $UR_{LRTP}^x < 1$ in chemical property space spanned by K_{oa} and K_{aw} (results for ChemRange). Lines are drawn to delimit property combinations for which $>90\%$ of the chemical will be present in one compartment only.

For LRTP, the contour plot looks distinctly different from that for P_{OV} . Here the number of cases with $UR_{LRTP}^x < 1$ are smallest in those regions where the chemicals partition in considerable amounts between two or three media (see Figure 5) and vice versa, largest where the chemical partitions to only one of the main compartments. This is interpreted as follows: In those regions where the chemical partitions to one compartment mainly, differences in models with respect to transport mechanisms in these compartments become very influential and model uncertainty becomes large. There are three such situations which have been identified before (OECD, 2004) and can be clearly recognized in Figure 5: (i) For chemicals mainly partitioning to air, the choice of transport- versus target region-focused LRTP definitions will strongly influence the ranking, (ii) For chemicals mainly partitioning to water, models that include transport in water such as ChemRange and Impact will yield considerably higher LRTP values, especially for long half-lives in water, and (iii) For chemicals partitioning strongly to particles in air, it makes a large difference whether particle-transport in air is included as a transport mechanism in the model or not, which is the case in the CEMC level II model. In addition, similarly as observed for P_{OV} , for $K_{aw} < -7$ and $K_{oa} > 6$ sorption to particles and dissolution in rain droplets, leading to washout from the atmosphere, strongly influence the LRTP

in air to the extent that these processes become more influential than degradation. This in turn leads to very low parameter uncertainty for chemicals in these regions.

Obviously these results, indicating the relative importance of parameter versus model uncertainty, depend on the uncertainty factors assumed for the substance parameters and on the choice of the models to be compared. As discussed, model differences are the decisive factor leading to different UR_{POV}^x in the case of P_{OV} . The parameter uncertainty is close to a constant value for most hypothetical chemicals. If the uncertainty factor for half-lives was reduced to 5 instead of 10, this would approximately halve $CV_{POV,para}^x$. Even for this unlikely case, model uncertainty would only exceed parameter uncertainty in 35% of all cases. Hence, the main conclusion that for P_{OV} parameter uncertainty is considerably more dominant than model uncertainty remains valid. The findings for LRTP are even less sensitive to reduced parameter uncertainty because model uncertainty already dominates in most cases. Here, the choice of the models is more influential. However the models were chosen such as to represent a good collection of those models currently in use for the determination of P_{OV} and LRTP in various legislative and regional contexts. In that sense, the selection is justified and representative of model differences that are likely to be encountered in practice.

4 CONCLUSIONS

The findings on the different relative magnitude of parameter versus model uncertainty for P_{OV} and LRTP allow identifying the most efficient measures to reduce uncertainty in P_{OV} and LRTP. For the calculation of LRTP it is crucial to understand the main model differences as laid out in Figure 1 and to know for which chemical property combinations they matter most. These differences in mind, the user should choose the model that is best suited for his purpose (see OECD, 2004). On a side note, it is interesting to observe that the models agree well for the chemicals they have originally been developed for, i.e., chemicals with typical multimedia behavior, and that they disagree most for chemicals that partition mainly to one compartment.

To reduce uncertainty in P_{OV} , which is dominated by parameter uncertainty, it is most fruitful to invest efforts on improving data on degradation rate constants. Also, the use of spatially resolved models might reduce the variance of P_{OV} to true parameter uncertainty in those rare cases where

spatially resolved fate data on degradation and partitioning is available.

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